PREPARATION AND CHARACTERIZATION OF BIOBASED THERMOPLASTIC STARCH/POLYPROPYLENE BLENDS FOR THERMOFORMING APPLICATION

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PREPARATION AND CHARACTERIZATION OF BIOBASED THERMOPLASTIC STARCH/POLYPROPYLENE BLENDS FOR THERMOFORMING APPLICATION

by

PANG MING MENG

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Material
AWS	Agricultural Waste Seed
AWT	Agricultural Waste Tuber
CS	Commercial Biobased Sample
DMA	Dynamic Mechanical Analysis
DOE	Design of Experiment
DSC	Differential Scanning Calorimeter
EB	Elongation at Break
FTIR	Fourier Transform Infrared Spectroscopy
HDT	Heat Distortion Temperature
MA-g-PP	Maleic Anhydride Grafted Polypropylene
MFI	Melt Flow Index
MD	Machine Direction
NTS	Native Tapioca Starch
PP	Polypropylene
TD	Transverse Direction
TGA	Thermogravimetry Analysis
TPS	Thermoplastic Starch
TS	Tensile Strength
UV	Ultraviolet
SEM	Scanning Electron Microscope
YM	Young's Modulus

LIST OF SYMBOLS

ρ	Density
wt	Weight percent
ΔH	Heat of fusion
χ_c	Degree of crystallinity
T_g	Glass transition temperature
T_m	Melting temperature
T_{max}	Onset degradation temperature
T_{onset}	Maximum decomposition temperature
t	Time
η_0	Zero shear viscosity
K	Material constant
M	Molecular weight
M_t	Percentage of weight gain at time t
W_d	Weight of dry sample
W_w	Weight of sample immersed in water
G’	Storage modulus
G’’	Loss modulus

PENYEDIAAN DAN PENCIRIAN BIOASAS ADUNAN TERMOPLASTIK KANJI/POLIPROPILENA BAGI APLIKASI PEMBENTUKAN BERHABA

ABSTRAK

Dalam kajian ini, termoplastik kanji (TPS) berasaskan sisa pertanian (iaitu, sisa pertanian benih, AWS dan sisa pertanian akar, AWT) beradun dengan polipropilena (PP) untuk menghasilkan sebatian bioasas. Penggunaan kanji yang berasaskan sisa pertanian boleh mengatasi isu pembuangan sisa, mengelakkan konflik penggunaan tanaman makanan manusia sebagai bahan mentah dan mempelbagaikan penggunaan sisa. Kanji ubi kayu (NTS) dan sampel bioasas komersil (CS) juga digunakan untuk perbandingan. Formulasi optimum dikenalpasti melalui reka bentuk eksperimen (DOE). Sebatian bioasas dihasilkan melalui pengekstrudan skru kembar, kemudian melalui proses pengekstrudan lembaran dan pembentukan berhaba. Adunan TPS/PP telah memenuhi syarat minimum 25% kandungan bioasas yang ditetapkan oleh pelbagai organisasi antarabangsa bioasas. Sifat bahan bioasas telah dikaji melalui ujian terma, fizikal, tensil, penyerapan air, biodegradasi aerobik, penanaman dalam tanah secara tertutup dan luar, pencuacaan dan jejak karbon. Kandungan amilopektin yang tinggi dalam adunan sisa pertanian (iaitu AWS/PP) lebih mudah terdedah kepada degradasi terma daripada bahan yang kaya amilosa (iaitu NTS/PP). Suhu degradasi onset kanji memberi impak secara langsung kepada suhu penguraian PP. Penambahan kanji ke dalam PP bukan sahaja menyebabkan kesan kekakuan seperti yang ditunjukkan dalam peningkatan modulus penyimpanan, ia juga menyebabkan pengenduran dalam matriks polimer dengan peralihan terma (iaitu, T_g) teranjak kepada suhu lebih tinggi. Sifat unggul tensil AWS/PP, terutamanya pemanjangan pada takat putus disebabkan daya lekat antara muka yang kuat seperti yang ditunjuk dalam mikroskopi elektron pengimbasan

(SEM) dan kesan pemplastikan oleh kewujudan protein dan lemak dalam serbuk AWS. Sifat bukan-Fickian telah diperhatikan dalam ujian penyerapan air, di mana terdapat serapan air yang tinggi dalam adunan kanji yang tinggi amilopektin (iaitu, AWS/PP) berbanding adunan yang disediakan daripada kanji yang tinggi amilosa (iaitu, NTS/PP). Peratusan biodegradasi aerobik yang tinggi untuk adunan yang tinggi amilopektin disebabkan struktur bercabang-cabang dan penyerapan air yang cepat. Amilopektin dengan struktur bercabang-cabang lebih senang dipecahkan oleh enzim berbanding amilosa yang berstruktur linear dan serapan air yang tinggi menggalakkan pertumbuhan mikroorganisme. Penanaman dalam tanah secara luaran mengalami kehilangan berat yang lebih tinggi dan kemerosotan sifat tensil berbanding dengan penanaman dalam tanah secara tertutup. Degradasi disebabkan oleh pencuacaan berlaku dengan cepat disebabkan kesan radiasi UV bergabung dengan pengoksidaan, kelembapan, suhu dan serangan mikrob. Kajian SEM menunjukkan retakan permukaan dan kehadiran mikroorganisme. Spektrum Inframerah Transformasi Fourier (FTIR) menunjukkan peningkatan dalam indeks karbonil sepanjang pencuacaan. Jejak karbon untuk dulang bioasas pembentukan berhaba didapati 20% lebih rendah daripada dulang talkum berisi-PP, disebabkan jejak karbon yang rendah bagi bahan mentah bioasas, suhu pemprosesan yang lebih rendah dan kitaran pembentukan berhaba yang singkat. AWS/PP merupakan bahan bioasas yang paling sesuai bagi aplikasi pembentukan haba berdasarkan pretasi yang baik dalam ujian tensil, peratusan biodegradasi yang tinggi, rintangan terhadap pencuacaan dan memiliki jejak haba yang paling rendah.

PREPARATION AND CHARACTERIZATION OF BIOBASED THERMOPLASTIC STARCH/POLYPROPYLENE BLENDS FOR THERMOFORMING APPLICATION

ABSTRACT

In this study, thermoplastic starch (TPS) derived from agricultural waste sources (i.e., agricultural waste seed, AWS and agricultural waste tuber, AWT) was blended with polypropylene (PP) to form a biobased compound. The utilization of starch-containing agricultural waste can provide a solution for the waste disposal issue, avoiding the conflict of using food crops starch as feedstock and diversify the usage of waste. Native tapioca starch (NTS) and commercially available biobased sample (CS) were also used for comparison. The optimum formulation was identified through a design of experiment (DOE). The biobased compounds were prepared by using twin-screw extruder, which later subjected to sheet extrusion and thermoforming process. The TPS/PP blends were able to meet the minimum 25% biobased content target as required by various biobased international organizations. The biobased materials behaviour were investigated through thermal, physical, tensile, water absorption, aerobic biodegradation, indoor and outdoor soil burial, natural weathering and carbon footprint study. The higher amylopectin content present in the agricultural waste starch blend (i.e. AWS/PP) was more susceptible to thermal degradation than amylose-rich material (i.e., NTS/PP). The onset degradation temperature of starch component has a direct impact on the decomposition temperature of PP. The addition of starch into the PP not only led to a stiffening effect and resulted in an increase in the storage modulus; it also affected the relaxation of the polymer matrix by shifting the thermal transition (i.e., T_g) to a higher temperature. The superior tensile performance of AWS/PP, particularly the

good elongation at break could be attributed to its good interfacial adhesion as shown in scanning electron microscope (SEM) and the enhanced plasticization effect by the presence of protein and fat in AWS powder. A non-Fickian behavior was observed for the water absorption test, and highest water uptake was observed for high-amylopectin starch blends (i.e., AWS/PP) compare to blends made with high-amylose starch (i.e., NTS/PP). The highest aerobic biodegradation percentage in amylopectin rich material can be explained with the branched structure and high water absorption behaviour. The branched amylopectin structure is easier to break down by the enzyme than linear amylose and high water uptakes encouraged the growth of microorganisms. The outdoor soil burial showed greater weight loss and deterioration in tensile properties as compared to indoor soil burial. Natural weathering degradation process occurred rapidly due to the combine effect of UV radiation with oxidation, moisture, temperature and microbial attack. The SEM micrographs revealed the formation of surface crack and presence of microorganisms. Fourier Transform Infrared Spectroscopy (FTIR) spectrum indicated an increase in the content of carbonyl index over weathering time. The carbon footprints of biobased thermoformed trays were 20% lower than talc-filled PP tray, as a result of the low raw material footprint of renewable input, lower processing temperature and shorter thermoforming cycle. AWS/PP is the most suitable biobased material for thermoforming application based on its excellent tensile performance, highest biodegradation percentage, resistance to natural weathering and lowest carbon footprint.

CHAPTER 1

INTRODUCTION

1.1 Background of Research

According to definition in ASTM D6852, a biobased material is an organic material containing carbon that has been derived from a renewable resource via a biological process. Renewable resources are available in recurring basis such as starch and cellulose. A biobased product can be partially or fully made from renewable resources as defined in ASTM D6852. According to biobased certification organizations such as United States Department of Agriculture (USDA) and Japan BioPlastics Association (JBPA), a minimum of 25% biobased content via the ASTM D6866 is usually required in order to certify a product as a biobased product. As consumers become increasingly concerned about the origin of their products, this has encouraged the development of biobased certification systems in different parts of the world to certify the origin of biobased products.

The objective of promoting biobased materials is to mitigate the global warming issue and to reduce the consumption of fossil resources. Global warming occurs due to the increase of greenhouse gases (GHG), specifically the release of carbon dioxide (CO_2) into the atmosphere, i.e. the greenhouse effect. The greenhouse explanation is based on the fact that the global mean temperature increase coincides with increasing emissions of CO_2 (and other GHG such as methane) from human activities. The concentration of CO_2 in the atmosphere has been trending up since 1800, from about 275 to 390 ppm in 2011 (Kutilek, 2011).

Global warming causes the melting of land ice, a rise in global sea level, the flooding of low-lying areas and thus making them uninhabitable. Global warming

also leads to extreme weather such as droughts or storms, a drop in the yield of agricultural and food production, human health issues, like heat shock, and indirect diseases, such as infectious diseases and allergies (Kurane, 2010). Higher ocean temperatures cause a reduce capacity for the dissolution of oxygen and may cause mass extinctions in the ocean (Gabel, 2011).

It has become the eco-responsibility of industries to create a sustainable society by encouraging the usage of biobased products. Innovative manufacturers are eyeing various agricultural wastes and by-products such as rice straw, empty fruit bunches, and cellulose, etc. as part of their biobased material development. By doing this, these companies are contributing in creative ways to resolve the environmental problems of waste disposal, cutting down the dependence on fossil fuels and subsequently reducing the emission of CO_2 into the atmosphere. The major problems associated with the utilization of agricultural wastes include poorer yield, supply issues, handling and processing costs (Sarkar et al., 2012). As a green plastic pioneer, NatureWorks has also announced that there is a future plan in place to make polylactic acid resin (Ingeo) from cellulosic raw materials, agricultural wastes and non-food plants (NatureWorks LLC, 2011).

Malaysia is a developing country and is not legally bound by the Kyoto Protocol agreement to reduce the GHG emissions (UNFCCC, 2011). However Malaysian government has voluntarily committed to a 40% reduction of its 2005 gross domestic product (GDP) emissions intensity levels by 2020 and, under these conditions, receives assistance from developed countries (The Star, 2009). United Nations Statistics show Malaysia's CO_2 emissions in 2005 stood at 183 million metric tons, or 7.0 metric tons per capita. As a comparison with neighbouring countries, CO_2 emissions in Singapore and Indonesia in 2005 were reported as 11.6

and 1.5 metric tons per capita, respectively (United Nations Statistics, 2012). One approach to cut down the carbon emission in the country is by encouraging the use of biobased products.

Starch is one of the most abundant and inexpensive renewable polymer. Starch consists of linear amylose and highly branched amylopectin chains. Starch can be plasticized under specific conditions, such as high temperature and shear to obtain thermoplastic starch (TPS) (Ning et al., 2007; Shi et al., 2007). In some studies, the granular structure of starch has not been completely disrupted by processing, as visualized by microscopic techniques (Ratto et al., 1999; Vaidya et al, 1995).

TPS has two main disadvantages compared to most plastics currently in use, i.e., poor mechanical properties and high water solubility. Starch itself is brittle and the tendency for it to retrogradate makes TPS rigid and unsuitable for daily application (Wang & Huang, 2007). Moreover, starch is hydrophilic and plasticized starch is water soluble. Its water solubility speeds up the degradation process and this moisture sensitivity again limits its application (Yu et al., 2006). One approach to improve the mechanical properties and reduce water sensitivity is the use of natural fibres to reinforce TPS (Prachayawarakorn et al., 2010). Another way to overcome these drawbacks is to blend TPS with synthetic polymers, such as traditional polyolefins (Chandra & Rustgi, 1997; Rodriguez-Gonzalez et al., 2003; Danjaji et al., 2002; Rosa et al., 2010). In this study, the biobased TPS was blended with polypropylene (PP) for properties improvement.

Starch is a hygroscopic material. During melt blending, the high moisture content of the starch gives rise to bubbles that weaken the mechanical properties. Thus, the processing of the TPS/PP can be a challenge in the conventional

equipment. The screw configuration and the devolatilization (removal of water content) step are very important to ensure the production of a homogenous and compact compound. The extrusion of the TPS/PP compound requires lower melt temperature than conventional polymer. High processing temperature (above 200℃) or excessive hold times can give rise to TPS degradation. A low shear screw configuration with high surface regeneration function is required to allow proper mixing and devolatilization during compounding process.

Plastic shaping processes, such as sheet extrusion and thermoforming, have become major processes with a growing range of applications, particularly in the packaging industry (Torres & Bush, 2000). The thermoforming process is in favour because it is more economical in the aspect of lower temperature and pressure requirement (no need to melt the material), moreover, a thermoformed mold is also cheaper compared to similar injection mold tools and is able to produce larger parts (Vantageplastics, 2011).

In the sheet extrusion process, the single-screw extruder melts the biobased compound and then shapes it by a sheet die into a single layer sheet. The pre-drying of the biobased material and the optimization of the processing parameters are very important to produce a uniform thickness sheet. A sheet with an uneven thickness will cause rough surface and inconsistent wall thickness of thermoformed parts.

The heating and cooling stage control in thermorforming are very critical for the production of quality formed part. The biobased TPS/PP produced in this study is considered as semi-crystalline polymeric material. It is important not to overheat the extruded sheet as the heating temperature is just slightly below the melting point for semi-crystalline materials (Schmidt et al., 2003). During the cooling stage, the molecule chains become more ordered, that is, their density increases and their

volume is reduced (crystallization shrinkage) (Endres & Siebert-Raths, 2011). As a result, the semi-crystalline polymers always tend to shrink more than amorphous ones. Thus, sufficient cooling of the formed part with forced air or a blower is needed in order to reduce warpage and distortion of the part after it is removed from the mold.

This research project can be divided into two parts. The first part contained the laboratory scale preparation of TPS from 3 different starch sources (i.e., high amylose, medium amylose and low amylose starch) and its blend with PP. A design of experiment (DOE) was carried out to determine the optimum loading of each component (i.e., starch, PP, plasticizer and compatibilizer). The second part of the study utilized this optimum formulation for the preparation of TPS from agricultural waste and its blend with PP. Native tapioca starch (NTS)-based TPS and commercial grade of TPS (denoted as CS) were also prepared for comparison purpose. This biobased TPS/PP blend was targeted to fulfill the international biobased body requirement of minimum 25%. The biobased compounds were subjected to sheet extrusion and thermoforming process to produce semi-durable tray for packaging application which can be recycled after end of life. The biobased TPS/PP blends with different amylose/amylopectin ratios were characterized for tensile, thermal, water absorption, soil burial and natural weathering degradation tests. The carbon footprint of the thermoformed tray was presented as well.

1.2 Problem Statement

Most of the studies on TPS reported the utilization of starch derived from food crops, such as potato, wheat, rice and corn, but not from agricultural waste. (Bikiaris, 1998; Li, G. et al., 2011; Prachayawarakorn et al., 2010; Sabetzadeh et al.,

2012; Swinkels, 1985). These types of starch sources are important staple foods for the human population, as they possess a high starch content of over 70%. As a result, the use of food crops as feedstock has led to an argument over food-feed competition (Kim & Dale, 2004). To avoid that conflict, this study focuses on the utilization of agricultural waste that can be converted into TPS.

Two types of starch-containing agricultural wastes have been identified: agricultural waste seed (AWS) and agricultural waste tuber (AWT). Both AWS and AWT can be easily obtained in Malaysia and within the neighboring countries, including Thailand and Indonesia. The AWS and AWT, with lower starch content (approximately 50 %), were used for the preparation of biobased TPS/PP blends. One of the challenges addressed by this study is that agricultural waste contains a lower starch content compared to a normal starch source, and it therefore may fail to attain the desired plasticity and degradability.

During the thermoplastic process, the strong action between hydroxyl groups of starch molecules was substituted by hydrogen bonds formed between plasticizer and starch, thus the starch was plasticized (Yang et al., 2006). However, in this study, a low volatile glycerol-based plasticizer is preferred over high volatile plasticizer (i.e., water), due to the challenges in processing with water-based plasticizer whereby water can evaporate fast and increase thermal breakdown (Lima & Andrade, 2010). The problem associated with the poor compatibility between the hydrophilic starch and hydrophobic polymer matrix (i.e., PP, PE) has been widely reported by previous researchers (Chandra & Rustgi, 1997; Wang et al., 2005). In this study, maleic anhydride grafted polypropylene (MA-g-PP), was added as a compatibilizer to improve the interfacial adhesion of TPS/PP blends.

In addition, the compounding process control, which include the raw material mixing and feeding, screw configuration, devolatilization setting, processing temperature and screw speed, determine the properties of the biobased compound. The biobased compound produced in this study will be used for the subsequent conversion processes, such as the sheet extrusion and thermoforming. To our best knowledge, the utilization of biobased TPS/PP blends in thermoforming application, particularly TPS derived from starch-containing agricultural waste is very rare (Shen et al., 2009). The challenge here is to produce a homogenous and compact compound, followed by a uniform extruded sheet which can meet the thermoforming criteria, such as its capability to form a deep-draw article of at least 5 cm in depth. The thermoforming grade material is targeted to have balance properties such as good stretching property (elongation at break above 50%), heat distortion temperature of at least 90℃ and low footprint, at the same time meeting the minimum biobased content of 25%.

The amylose-to-amylopectin ratio can influence the properties of the materials. Normal native starch generally consists of 25% amylose and 75% amylopectin (Baik et al., 2010). It is reported that preference is on the amylose-rich material since it showed better thermal stability, superior strength and lower water absorption compared to amylopectin-rich material (Mani & Bhattacharya, 1998a; Ke et al., 2003; Chaudhary et al., 2009). In this study, the starch-containing agricultural waste was showing lower amylose content than normal native starch, and one can even contain as low as only 1% amylose with the rest being amylopectin. Thus, it is an interesting field of study to investigate the degradation performance of the agricultural waste-based TPS/PP blend with different amylose/amylopectin ratios.

The degradation studies such as the soil burial tests and natural weathering are critical to enable prediction on the product shelf-life and the end-of-life option.

The promotion of the biobased materials is to mitigate the global warming. Previous research findings indicate that the CO_2 emissions generated by the production of biobased polymers are significantly lower than the amount generated by the production of petrochemical-based polymers (Akiyama et al., 2003; Narayan, 2009). However, there is limited literature available for the carbon footprint calculation of a thermoformed article. In this study, the carbon footprint of the thermoformed tray made from biobased material was calculated according to Publicly Available Specification (PAS) 2050 methodology. The calculation of a product's carbon footprint is important, as it can help the manufacturer understand their key carbon-intensite areas that have the greatest impact on overall footprint and prioritize areas for emission reduction.

1.3 Research Objectives

1. To prepare and characterize TPS from non-edible starch source, i.e., agricultural waste and its blend with PP for semi-durable thermoforming packaging application. The TPS/PP blends must be able to achieve a balance of properties and meeting the minimum biobased requirement of 25%.

2. To investigate the mechanical, thermal and morphological behaviors of the TPS/PP blends.

3. To study the degradation behaviors of the TPS/PP blends during water absorption, aerobic biodegradation, soil burial tests (indoor and outdoor environment) and natural weathering.

4. To study the carbon footprint of thermoformed trays made from biobased TPS/PP blends.

1.4 Thesis Outline

This thesis is organized and divided into five chapters:

Chapter 1 briefly introduces the research background of TPS/PP as a biobased material, the problem statements and objectives of the research work.

Chapter 2 presents the literature review on biobased plastics, particularly information on TPS blends, including the background theories adopted in this research project, international biobased standard requirements and previous research findings on TPS blends.

Chapter 3 covers the material specifications, methodology and equipment used for the development and characterization of biobased TPS/PP blends.

Chapter 4 presents the results and discussion of the study. This covers the DOE analysis to obtain the optimized formulation, the application of the formulation in twin-screw compounding, and the subsequent shaping processes, i.e., sheet extrusion and thermoforming. The characterization studies of the compounds and extruded sheets, including the thermal analysis, water absorption, soil burial and natural

weathering tests. The carbon footprint measurement of the thermoformed trays is presented in the last part of this chapter.

Chapter 5 summarizes the research project findings and recommendations for future works.

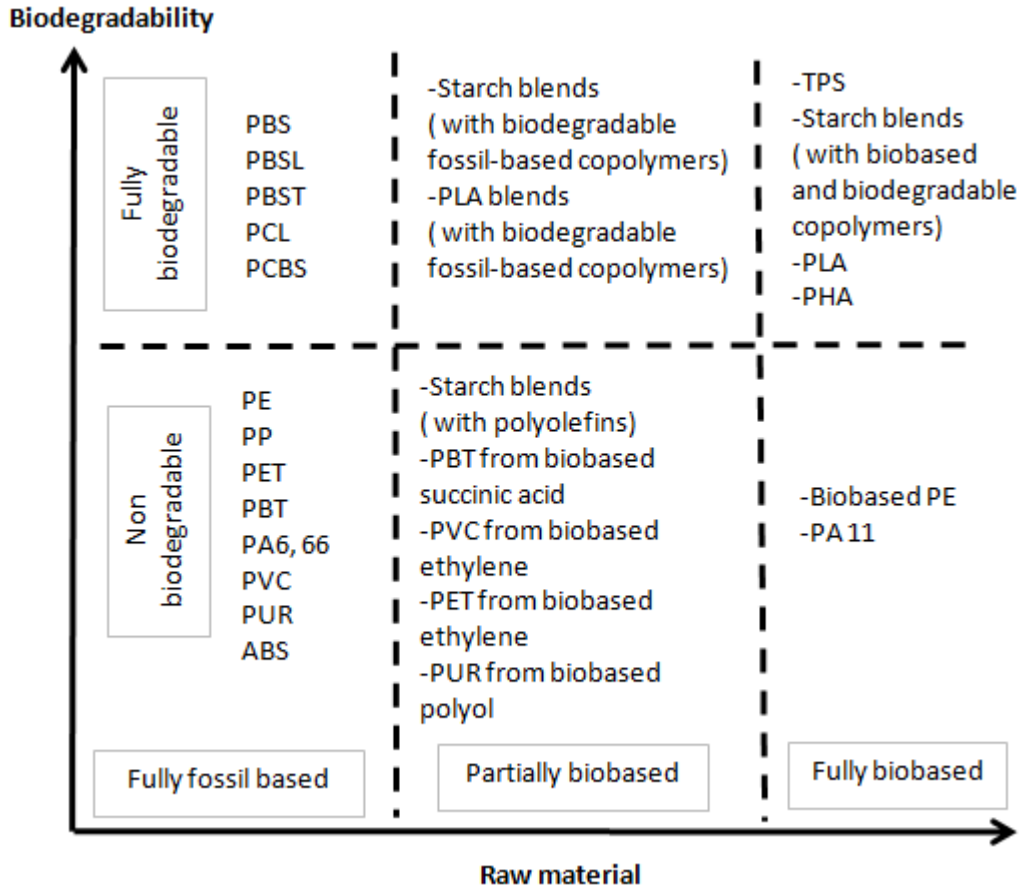
CHAPTER 2

LITERATURE REVIEW

2.1 Biobased Plastics Overview

Biobased plastics are man-made organic macromolecules derived from renewable resources and used for non-food purposes, such as for moulding plastic products (Shen et al., 2009). The awareness of climate change, environmental concerns and the hike in fossil fuel prices are important drivers for the development of biobased plastics. Some early attempts on promoting biobased plastics started in the late 1970s through the introduction of simple products, such as thermoplastic starch and starch/polyolefin blends (Griffin, 1977, 1978; Otey & Westhoff, 1979, 1982).

Biobased plastics are defined as plastics that are fully or partially produced from renewable raw materials, and they can be either fully biodegradable or non-biodegradable. Figure 2.1 shows the relationship of a raw material source (fossil or biobased) with its biodegradability features (fully or non-biodegradable) (Shen et al., 2009). In this work, the starch blends with PP fall within the category of partially biobased and non-biodegradable. Depending on the field of application, the new generation of biobased plastics is to move away from degradability and to move towards resistance, such as bio-PE, which is suitable for the automotive industry, where durable plastics are in demand (Endres & Siebert-Raths, 2011).



Abbreviations: PBS = polybutylene succinate; PBSL = polybutylene succinate-co-lactate; PBST=polybutylene succinate terephthalate, PCL=polycaprolactone. PCBS= poly(l-cystine bisamide-g-sulfadiazine), PBT=polybutylene terephthalate, PET=polyethylene terephthalate, PUR= polyurethane, PA= polyamide, PVC= polyvinyl chloride, ABS= acrylonitrile butadiene styrene, TPS = thermoplastic starch, PLA= polylactic acid, PHA= polyhydroxyalkanoates.

Figure 2.1: Raw material source and biodegradability (Shen et al., 2009)

The world production capacity of biobased plastics is growing from 0.36 mega tonnes (Mt) (2007) to 0.72 Mt (2010), and it is projected to reach 3.5 Mt by year 2020 (Shen et al., 2009). As shown in Table 2.1, the estimated production capacity in the order of the highest volume starts with starch plastics (1.3 Mt), followed by PLA (0.83 Mt), biobased PE (0.61 Mt), PHA (0.44 Mt), biobased monomers of epichlorohydrin (0.21 Mt) and others, such as biobased PUR and PA11 (0.06 Mt) (Shen et al., 2009). The demand for biobased biodegradable plastics will continue to grow to address the issue of waste disposal, while biobased non-

biodegradable plastics are showing good prospects as substitutes for the current polyolefin for durable applications.

Table 2.1 : Estimated worldwide biobased plastics production in 2020 with classification of "Biodegradable" and " Non-biodegradable" according to relevant company announcements (the most recent data received in March 2009) (Shen et al., 2009)

Category	Biodegradable	Non biodegradable	Total
Starch plastics	780	519	1299
PLA	830	0	830
PHA	440	0	440
Biobased ethylene	0	610	610
Biobased monomers	0	210	210
Others	25	35	60
Total (10^3 tonnes)	2075	1374	3449
	60%	40%	100%

Starch plastics are one of the key players in biobased plastics, which are used in the packaging industry, furniture and office equipment, automobile components and consumer electronic parts. Some examples of world leading starch plastics manufacturers include Novamont, BIOP, Cereplast and Teknor Apex. The sources of plant starches include corn, potato, tapioca, wheat and rice. However, manufacturers are facing challenges in marketing the starch plastics due to several reasons, some of which are the lower performance of the starch blends compared to conventional plastics, higher production costs, and competition with human food, since starch is now also used as feedstock for industries. The agricultural land use issue, where land previously used for food cultivation is now being used to produce biobased feedstock, has led to the loss of biodiversity (Rathmann et al., 2010; Shen et al., 2009). One of the solutions is to utilize agricultural waste as raw materials in order to solve the waste disposal problem, the land use issue and also to diversify the usage of the waste.

2.2 Starch

Starch is a renewable resource, where it can be easily replenished within a predictable time frame during the human life span (6 – 12 months). Starch granules are mainly found in roots, fruits, stems, seeds and tubers of plants. Sources of starch include corn, cassava, potato, wheat and rice (Xie et al., 2012). The total annual world production of starch was approximately 60 million tonnes in 2006, with corn dominating the market with a 73% share, followed by cassava, wheat and other crops (Maningat et al., 2009).

Starch is a heterogeneous material made of two microstructures – amylose and amylopectin (Li, M. et al., 2011). Native starch generally consists of approximately 25% linear amylose and 75% branched amylopectin. Figures 2.2-2.3 illustrate the molecular structure of amylose and amylopectin, respectively (Moad, 2011). Amylose is essentially a linear structure of α-1, 4-linked glucose units, and this linear structure makes its behaviour more closely resemble that of conventional synthetic polymers. However, its molecular weight of about 10^6 is 10 times higher than that of conventional synthetic polymers. Amylopectin is a branched polymer with short α-1,4 chains linked by α-1,6 bonds, and its high molecular weight of 10^8 tends to reduce the mobility of the polymer chains (Liu et al., 2009). Previous studies reported that high amylose materials showed superior strength and strain at break compared to high amylopectin-rich materials (Van Soest & Essers, 1997; Thuwall et al., 2006; Chaudhary et al., 2009). High amylose starch films exhibit better thermal and mechanical properties due to the linear and flexible structure of amylose chains. In addition, the retained granular structure in the high amylose films after extrusion is very stable and rigid, and thus may act as a self-reinforcement agent (Li, M et al., 2011).

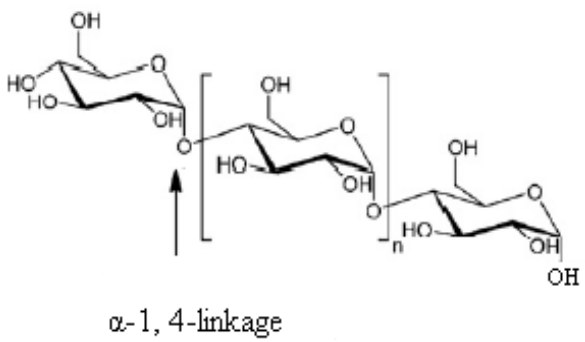


Figure 2.2: Amylose (Moad, 2011)

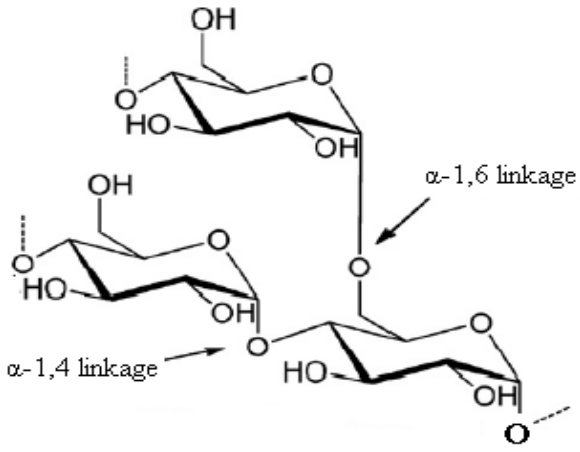


Figure 2.3: Amylopectin (Moad, 2011)

Most native starches are semi-crystalline, having a crystallinity of 15 to 45% (Zobel, 1988). The amylose and the branching points of amylopectin form amorphous regions. Meanwhile the short branching chains in the amylopectin are the main crystalline components in starch (Liu et al., 2010). Starch granules exhibit hydrophilic properties and strong inter-molecular association via hydrogen bonding due to the presence of the three hydroxyl groups in the granule (Bastioli, 2005).

2.3 Starch Modification

Starches can be classified into two types: native and modified. Native starches are produced through the separation of naturally occurring starch from grains and tubers while retaining the original structure. They can be directly applied to produce food or for other industry usages (paper, textiles, pharmaceuticals, cosmetics, mining, etc.). Gelatinization happens when starch granules are heated in a water medium, causing swelling of the starch granules, leakage of amylose and the disruption of the ordered structure (Blaszczak et al., 2007). However, the industrial and food applications of native starches are restricted because of their tendency to retrograde (changes occur in the starch after gelatinization, where the starch molecules re-associate and form an ordered or crystalline state) and undergo syneresis (water is forced out of the gel structure) (Rosalina & Bhattacharya, 2002; Liu et al., 2007).

Besides native starches, there are also specialty starches which can only be obtained from genetic plant variants, such as high amylose starches and waxy starches. A high amylose starch is produced from high specialty amylose corn with an amylose content of between 50%-90% (Plantic Technologies, 2011). Waxy starch, which contains >99% amylopectin, is produced from waxy maize. Waxy starches do not form gels and do not retrograde readily. High amylose starches retrograde more extensively than normal starches and are less digestible.

Native starches can undergo physical treatment (using heat or moisture), and enzymatic or chemical modifications (i.e., acetylation, esterification, etherification, oxidation and hydroxypropylation), which can convert the native starch into another form of starch called modified starch (Radley, 1968; Bae & Lim, 1998). Modified starch is produced to enhance the properties of starch, such as decreasing the

retrogradation tendency for gel forming, increasing the hydrophilic property, increasing the shear stability, and changing the gelatinization time which helps to expand its usage in industry. The cost of modified starch is generally higher than normal starch due to their specialty source or modification process.

2.4 Starch Source from Agricultural Waste

Agricultural waste refers to substances or objects generated by agricultural activities which are required to be discarded. Agricultural waste, such as oil palm fruit bunches, rice husks, cassava bagasse, sugar cane bagasse, coconut shells, coffee husks, barley husks, rice bran, apple pomace, corncobs, soursop seeds, etc., are becoming increasingly popular choices as raw materials in bioprocesses or for turning waste to energy (Singhania et al., 2009). Agricultural waste utilization can be a creative way to resolve the environmental problem of waste disposal, while generating a side income for the farmer. Robinson et al. (2002) investigated the use of two agricultural waste residues, barley husks and corncobs, for dye removal applications. Daifullah et al. (2003) studied the utilization of rice husks as a sorbent material for waste water treatment. Gao et al. (2007) investigated the utilization of rice bran as a low cost nutrient source for fermentative lactic acid production.

Some of the agricultural wastes do contain a certain amount of starch but the starch level is usually low (≤ 50%) and the handling of the agro residues is not hygienic for human food applications. The starches that are available in the market, like food grade corn starch and tapioca starch, generally have a starch content of more than 85%. Besides the low starch content issue, agricultural waste is also found to have a higher fibre content, which is not suitable for the human digestion system. As a result, the starch-containing agricultural waste is usually used for animal feed

and other non-food related applications, like the textile, printing, explosives and mosquito coil manufacturing industries (Yimmongkol et al., 2009; Wizna et al., 2009; Joshi & Sandhu, 1996).

In this research project, 2 types of starch-containing agricultural wastes which are in constant supply have been identified. The starch-containing agricultural waste will replace the native starch to be used for TPS development. The benefits of using the starch-containing agricultural waste include:

1. Low cost, since it is from waste.
2. Renewable resource.
3. Avoids human food competition.
4. Diversifies the usage of agricultural waste by making it into a biobased plastic.
5. Low carbon footprint as it only involves a simple process.
6. Resolves the issue of disposing.

2.5 Polypropylene

PP, which is from the polyolefin family, is semi-translucent and milky white in colour. PP is a linear polymer with propylene monomers of $(CH_2\text{-}CHCH_3)_n$ chains, which are packed together in the order of a crystalline structure. However, the chains may be entangled or imperfect (branching), so the structure is not completely regular, and can be described as a semi-crystalline polymer (Tripathi, 2002). PP is an extremely versatile plastic with excellent fatigue, high temperature resistance, chemical and electrical resistance, and a good balance of strength and stiffness. PP is a lightweight thermoplastic with a density of 0.9 g/cm^3. However, PP is unstable in the presence of oxidation conditions and UV radiation (Rosato, 1993).

The production of PP utilizes Ziegler-type catalysts and the newer metallocene-based materials, which offer better control and specialty properties. The major product is isotactic PP. Through the Ziegler-type catalysts, various quantities of atactic PP are included as by products. In general, a higher isotacticity index will result in a higher modulus and yield stress, but lower elongation at break. The advent of metallocene catalysts makes the arrangement of tacticities and structures possible, and thus a range of compositions that were not easily prepared before, such as syndiotactic polypropylene, are now possible (Sperling, 2006).

There are a few grades of PP available in the market; each meets particular requirements and costing. PP homopolymer is the most common general purpose grade with a single type of repeating unit that can be used in various applications. PP block copolymer is made from two or more monomers, usually incorporating 5-15% ethylene, with enhancement in impact properties and toughness. Another grade is PP random copolymer, where the co-monomer units are arranged randomly (as distinct from discrete blocks) along the PP long chain molecule. PP random copolymer, which typically contains 1-7% ethylene as a co-monomer, exhibits a lower melting point, better flexibility and greater transparency (Plastipedia, 2011). In this research project, homopolymer PP is selected to blend with starch-containing agricultural waste. The introduction of the thermoplastic starch (TPS) and starch blends of synthetic polymers will be discussed in the following topic.

2.6 Thermoplastic Starch

Starch itself is brittle and hydrophilic. The melting point of native starch is higher than the thermal decomposition temperature, and this means starch granules decompose before melting (Shen et al., 2009). As a result, starch cannot be processed

in the same manner as conventional polyolefin-based thermoplastics. However, by adding in a suitable plasticizer, such as a low molecular mass alcohol or polyols, like glycerol, in the presence of high temperature and shear, the starch will melt below the decomposition temperature, creating a material named thermoplastic starch (TPS) or plasticized starch (DeLeo et al., 2011). Water is not a good plasticizer because it can evaporate during the process and increase the degree of thermal breakdown (Lima & Andrade, 2010). The retrogradation (recrystallization) of the starch is the main issue that restricts its practical use in daily applications as it will become rigid and brittle during long storage time and will lose the value of its usefulness (Wang & Huang, 2007).

Scientists have experimented on different types of starches and turned them into thermoplastic materials. Starch sources that have been reported and even patented include native starches made from corn, tapioca, maize, wheat, rice, sorghum and sago, or processed starches, such as gelatinized starch, modified starch ethers and esters, hydroxylalkyl starch, oxidized starch, waxy starch and high amylose starch etc. (Wang et al., 2010a & b; Wang et al, 2003; Lay et al, 1992; Rosa et al., 2009). A mixture of two or more types of modifications can also be used in the experiment to achieve the desired properties. However, modified starch is generally more expensive than unmodified starch. For example the cost price of high amylose starch is 3 times higher than that of native corn starch.

Anderson & Hudson (2001) discussed the very details of the classification of TPS in the US patent. Native starches do not typically behave as thermoplastic materials but must be heated in the presence of plasticizers in liquid form. The plasticizers that are used to assist in the formation of starch melts can be either highly volatile liquids, like water, or low volatile liquids, like glycerol. Starch granules

generally have a coating or outer shell that encapsulates the more water soluble amylose and amylopectin chains inside. This coating makes unmodified native starch granules insoluble in cold water. However, when the starch granules are heated in the presence of water or a polar solvent, the solvent is able to soften and penetrate the outer shell and cause the inner starch chains to absorb water and swell. If the swelling continues, the outer shell will rupture and cause the irreversible gelatinization or structural breakdown of the starch granules. In this patent, starch melts using water as the plasticizer have been referred to as "destructurized starch." Starch is said to be destructurized or gelatinized because it has been dissolved or melted in the water and will not return to its original granular state. However, the use of "destructurized starch" as commercial TPS material is not popular due to difficulties in processing encountered with water, poor mechanical properties, moisture sensitivity, retrogradation over time as moisture loss and poor dimensional stability.

A second approach to producing a TPS material is to replace the water plasticizer with a low volatile plasticizer or higher molecular weight plasticizer that is not volatile. This low volatile plasticizer must be able to melt the starch to form a thermoplastic below the decomposition temperature. Examples of low volatile plasticizers include glycerol, polyalkylene oxides, alcohols and citrates. As per definition by Anderson & Hudson (2001), a low volatile plasticizer has a vapour pressure of less than 1 bar at the melting temperature of the TPS composition, while a volatile solvent, like water, will have a vapour pressure that is greater than 1 bar at the melting temperature of the TPS composition. A TPS material, in which most or all of the water has been replaced by a low volatile plasticizer either before or during processing, has been referred to as a "thermoplastically processable starch" or

"thermoplastic starch (TPS)". A TPS produced from low volatile plasticizers is capable of keeping the starch more amorphous over time, and is claimed to be more stable, flexible, less crystalline and less brittle compared to destructurized starch. Water tends to migrate into and out of destructurized starch by evaporation under ambient conditions to form crystalline starch; while low volatile plasticizers tend to remain more closely associated with the hydroxyl groups of the starch molecules over time. So by remaining interposed between the starch polymer chains within the composition, this low volatile plasticizer can inhibit recrystallization and retrogradation of the starch chains compared to more volatile plasticizers, like water.

Another approach to make TPS is to blend a small quantity of water together with a low volatile plasticizer, such as glycerol, to form a starch melt. The water can be removed during processing by a degassing procedure before cooling and solidification (Bastioli et al., 1993 & 1995).

2.7 Starch-Filled Plastics

The attempt to use starch to prepare starch films started as early as the 1960s (Lloyd & Kirst, 1963), but the production of whole starch films has never achieved large-scale commercial success because the films are brittle after the plasticizer leaches out and are greatly affected by moisture (Otey & Westhoff, 1979). One of the attempts made to achieve the desired mechanical properties and improve the moisture sensitivity was to blend starch with plastic. In the 1970s, Griffin (1977) already explored the utilization of starch granules as biodegradable fillers for synthetic polymers, such as LDPE. This ductile film can be prepared up to 15 wt% starch content, and once the starch concentration exceeds 30 wt%, the properties of the product will not be satisfied (Griffin, 1977). Otey & Westhoff (1979)

successfully prepared a starch-EAA (ethylene acrylic acid) film either from the casting, extruding or milling method. This biodegradable synthetic film is useful for agricultural mulch and heat sealable packaging as it is flexible and water resistant.

Research activities on starch-filled plastics have continued to grow even until the 21st century particularly. The interest in starch is due to the abundant sources and the fact that it is inexpensive. Moreover, starch can impart partial biodegradability into the blend system. Research works are being carried out to enhance and improve the blend system from the composition and processing matter. According to Mani & Bhattachary (1998a), in order to replace the common thermoplastics in commodity applications, the starch blends must be processable in the existing standard equipment, and must provide comparable mechanical properties and stability to the non-degradable thermoplastics they replace. Some of the recent research works by DeLeo et al. (2011) revealed that the addition of clay, which acts as a reinforcing component, can improve the tensile strength and modulus of the plasticized starch/PP blends. The insertion of starch as a filler into PP showed an immiscible blend under a morphological study by using scanning electron microscopy (SEM). Another study showed the decrease in mechanical properties and viscosity of the starch/PP blends with an increase in the starch volume fractions (Azhari & Wong, 2001).

Ramis et al. (2004) prepared blends of PP/starch with a Brabender Plasticorder. The samples were tested for biodegradability under the soil burial test for a 1-year period and the results showed that biodegradation only affected the starch but not the PP. Zuchowska et al. (1999) studied the degradation behaviour of polyolefin-starch blends (PP or PE with plasticized starch), and reported that changes to the crystallinity and the heterogenity of the semi-crystalline polyolefin matrix

caused by chemical and physical degradation processes can affect the mechanical behaviour of the blends.

Bash et al. (2009) disclosed the processing method to make polyolefin compositions comprised of biobased starch materials. In this invention, polyolefin refers to PE, PP, polybutene and combinations thereof. The polyolefin is blended with starch, a compatibilizer and a plasticizer to produce a starch-polyolefin composition. The use of a compatibilizer in the polyolefin and starch blend formulation is to enhance the interfacial adhesion between the polyolefin and the starch.

The single step extrusion method is adopted to first mix the polyolefin with a compatibilizer as the first mixture, and then to mix the starch with a plasticizer to form the second mixture. The first mixture is fed into the main feeder of an extruder followed by the second mixture from a side feeder located downstream. The blended mixtures are eventually extruded from the extruder to form a homogenous extrudate. The proprietary extruder screw and barrel configuration setting are applied to handle the large amount of vapour generated from the starch mixture.

According to Bash et al. (2009), a plasticizer is any material that can soften and reduce the rigidity of plastic to make it more flexible. It is believed that plasticizers increase the flexibility of polymeric materials by increasing the free volume within the material. Plasticizers randomly dispersed within the polymer chains interfere and impede the ability of the polymer chains to align and to be packed into an ordered structure.

Plasticizers can be divided into 2 groups: external and internal plasticizers. External plasticizers are low volatile substances that are added into polymers during compounding. The molecules of the plasticizer interact with the polymer chains, but